UNCLASSIFIED

AD NUMBER
AD288106
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; JUL 1962. Other requests shall be referred to Rock Island Arsenal, IL.
AUTHORITY
RIAL ltr, 24 Apr 1967

THIS PAGE IS UNCLASSIFIED

UNCLASSIFIED

AD 288 106

Reproduced by the

ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA

UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

288 106

[redacted] MUST [redacted] REMOV[redacted]ROM THIS RE PORT WH[redacted]ED OR DISTRIBUT ED [redacted]SIDE THE [redacted]MENT OF DEFENSE.

CATALOGED BY ASTIA AS AD No. 288106

Rock Island Arsenal Laboratory

TECHNICAL REPORT

DEVELOPMENT OF FLEXIBLE INSULATION FOR SOLID PROPELLANT ROCKET MOTOR CASES

By

R. E. Ofner

and

D. H. Sale

Department of the Army Project No. 593-32-008

Ordnance Management Structure Code No. 5010.11.843

Report No. 62-2366 Copy No. ______

IEL 1-9-100-5 Date 6 July 1962

THIS REPORT MAY BE DESTROYED WHEN NO LONGER REQUIRED FOR REFERENCE

NO OTS

The findings in this report are not to be construed as an official Department of the Army position.

Report No. 62-2366

Copy No. ____________

DEVELOPMENT OF FLEXIBLE INSULATION FOR SOLID PROPELLANT ROCKET MOTOR CASES

By

R E Ofner

R. E. Ofner

and

D. H. Sale

D. H. Sale

Approved by:

A. C. Hanson

A. C. HANSON
Laboratory Director

6 July 1962

Department of the Army Project
No. 593-32-008
Ordnance Management Structure Code
No. 5010.11.843

Rock Island Arsenal
Rock Island, Illinois

ASTIA Availability Notice:

Qualified requesters may obtain copies of this report from ASTIA.

ABSTRACT

The development of flexible, solid propellant rocket motor case insulation is ~~discussed~~. Data are presented for insulation based primarily on butadiene/styrene and butadiene/acrylonitrile copolymers. The oxyacetylene torch test currently being standardized by the Flame Ablation Test Group of Section III-L of ASTM Committee D-20 was the principle screening tool used in the study.

Vulcanizates were compounded using a variety of fillers and filler combinations including salts, resins and fibers. The selection of these fillers was based on such properties as heat stability, ability to form char, heat capacity and their known ability to reinforce rubber. As a result of these studies, a material was developed which static motor tests show to have promise as a flexible material for case insulation. This material was based on a butadiene/acrylonitrile-phenol furfural-asbestos composition.

Other promising materials which are reported are based on two types of liquid butadiene/styrene copolymers and a butadiene/acrylonitrile-polyvinyl chloride blend.

RECOMMENDATIONS

It is recommended that a double bladed, Sigma type mixer be obtained in order that more uniform mixes of liquid polymers and fillers can be obtained without destroying the integrity of the filler itself.

It is recommended that commercially available liquid polymers be evaluated with long fiber asbestos as a filler in order to determine the superiority of one polymer over another.

The best insulation material developed to date in this study is a butadiene/acrylonitrile-phenol furfural-asbestos vulcanizate. It is recommended that a study be conducted to optimize this composition as to quantity and types of ingredients; for example, it might be possible to substitute a liquid polymer in place of the solid polymer.

Despite the poor elongation of resin filled insulation materials, the good insulating ability and erosion resistance of these vulcanizates warrant their further study. It is recommended that special efforts be made to evaluate fully the flexible resins developed by Atlantic Research Corporation under Contract #DA-036-ORD-3325RD as well as commercially available flexible resins.

DEVELOPMENT OF FLEXIBLE INSULATION FOR
SOLID PROPELLANT ROCKET MOTOR CASES

CONTENTS

DEVELOPMENT OF FLEXIBLE INSULATION FOR SOLID PROPELLANT ROCKET MOTOR CASES

OBJECT

To develop improved, flexible, thermal case insulation for solid propellant rocket motors.

INTRODUCTION

Lighter weight structural materials and more efficient propellants are among the major factors which are expected to improve the performance of solid propellant rocket motors. Concomitant with the use of these materials is the need for more efficient rocket motor insulation. The lightweight metallic and plastic case materials generally suffer from low tolerance to heat. The super propellants burn for several minutes at very high temperatures and produce high pressures and erosive combustion products. These factors all indicate the need for improved insulation. Superior insulation is especially needed for rocket motors which employ end-burning grains. Batchelor et al[1] point out that "the capability of rockets using end-burning grains can be limited by the motor case insulation because this material must survive exposure to the hot gases for the total duration of the firing."

Case insulation must possess the obvious characteristics of heat and erosion resistance in order to withstand the severe operating environments but in addition must exhibit the less obvious property of flexibility. The need for flexible case insulation has been cited by only a few workers in the open literature. Batchelor et al[1] state that "the liner [insulation] need not add mechanical strength to the case, but it must maintain its integrity while being strained to conform to the case deformation which occurs at initial pressurization and may reach 0.8 percent." Batchelor et al[2] further state that "the selection of rubber binders is often prompted by a realization that flexibility and reasonable elongation in a motor case insulation is generally desirable and often imperative." Shapiro and Hughes[3] describe rubber based insulation which has an ultimate elongation of 600 percent. This very high elongation was not the goal of these workers, it was merely the value obtained for the insulation which they had developed.

What degree of flexibility is required in case insulation? It would appear that the state of the art has not advanced sufficiently to provide answers to this question.

It is the opinion of the authors that Batchelor's value of 0.8 percent elongation is too low and does not provide a margin of safety. The 600 percent value of Shapiro and Hughes seems to be unrealistically high.

It has not been the purpose of the present study to determine the optimum degree of flexibility for case insulation nor has the work been pointed toward any particular rocket motor system. The primary aim has been the development of insulation materials having maximum flexibility and minimum density, with both of these properties moderated to provide insulations consistent with the fundamental requirements, namely, resistance to flame and erosion.

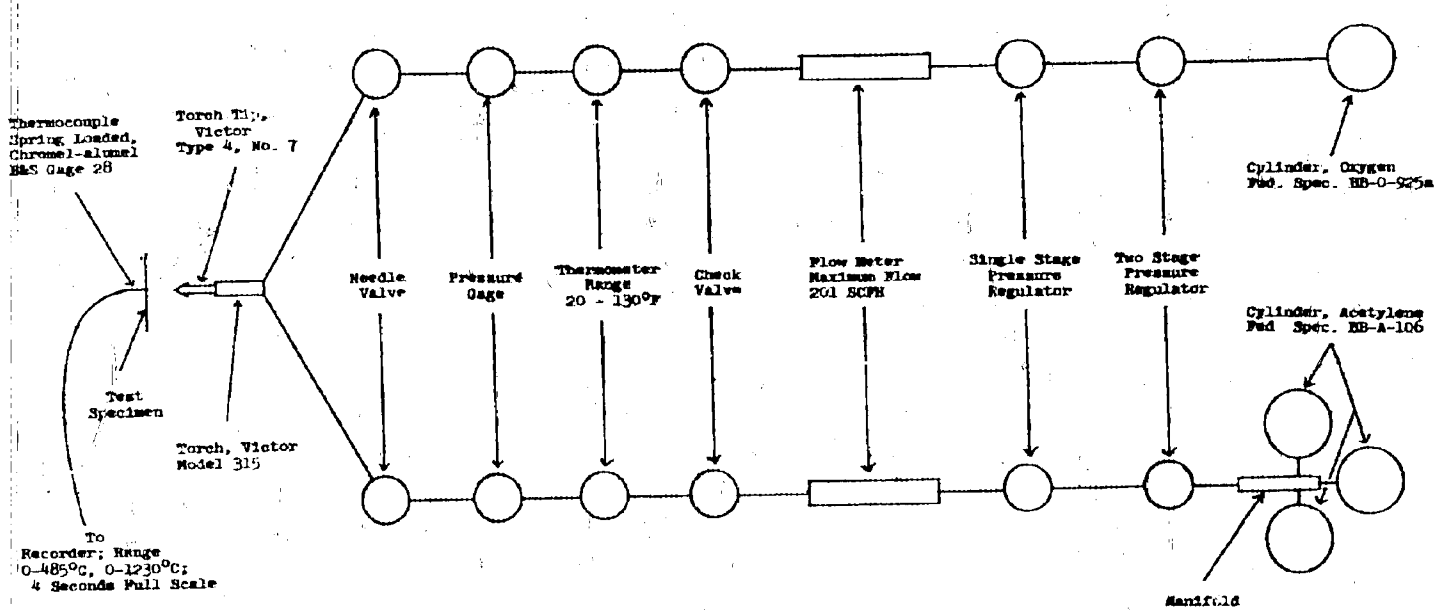
The many desirable features of case insulation, viz., compatibility with and bondability to grain and case, ease of manufacture from commercially available materials and high degree of reliability during long term storage have been kept in mind but have not been the main guidelines for the development work reported herein.

A major difference exists between the work reported herein and the earlier work[7] in that the test method used here is much more severe.

PROCEDURE

Screening of candidate insulation materials was performed with an oxyacetylene torch test. A schematic diagram of the test equipment is shown in Figure 1 and test conditions are presented in Table I. The equipment and procedures duplicate those of the test currently being standardized by the Flame Ablation Test Group of Section III-L of ASTM Committee D-20. Further details pertinent to this type of test have been published[4] by the Naval Ordnance Laboratory, the agency largely responsible for the current efforts to standardize the torch test.

The effectiveness of candidate insulation materials was measured by two test criteria. One was the rate of temperature rise on the back side of the specimen while the front side was exposed to the oxyacetylene torch flame. The other was the time required for the flame to burn through the specimen. The results of the tests obtained in such manner are reported as a performance index and an erosion rate. The index, referred to as P_{200}, is computed by dividing the time (seconds) required for the specimen back side to reach 200°C by the original specimen thickness (centimeters) and by the specific gravity. The erosion rate, E, is computed by dividing the original specimen thickness (mils) by the burn through time in seconds. It should be noted that high



SCHEMATIC OF RIA OXYACETYLENE TORCH APPARATUS

FIGURE 1

TABLE I

TORCH TEST OPERATING CONDITIONS

Oxygen flow rate, standard cubic feet/hour (SCFH),	127
Acetylene flow rate, SCFH,	97
Volume ratio of oxygen to acetylene,	1.3
Impingement angle between flame and specimen, degrees,	90
Specimen size, inches,	4 x 4 x 1/4
Distance from torch tip to specimen, inches,	3/4
Temperature of oxygen and acetylene, °C.,	24±3
Method of determining moment of burn through,	visual

values of P_{200} and low values for E are indicative of good insulation properties. Unless otherwise noted, the performance indices and erosion rates reported in this work are the average of two tests. The average variance of the performance index is ±3 points, that of the erosion rate about ±0.2 points.

Those materials which exhibited excellent thermal insulation capabilities during the screening test were further evaluated in static rocket motor firing tests conducted by the Allegany Ballistics Laboratory (ABL) and the Atlantic Research Corporation (ARC) at their respective test facilities. Details of the static firing test methods have been published in a classified report[5].

Formulations and curing conditions for all compositions tested are given in Table II. Test specimens were molded in a four cavity mold.

Unless otherwise noted, all compounds were mixed, cured and tested for stress-strain properties in accordance with the applicable ASTM[6] procedures.

RESULTS

One of the major findings of the earlier work[7] on case insulation conducted at the Rock Island Arsenal Laboratory was that the behavior of unfilled (gum) rubber vulcanizates, when tested in an oxyacetylene flame, depended upon the type of polymer present in the vulcanizate. This observation was based on data obtained with an oxyacetylene torch test similar in most respects to the ASTM proposed standard test described in Figure 1 of this report but utilizing a lower velocity flame which burned at a cooler temperature. In an effort to determine whether the higher velocity, hotter flame was also capable of differentiating among the insulation abilities of various gum vulcanizates, a portion of the earlier work on gum vulcanizates was repeated with the ASTM proposed test. The results obtained with the two torch tests and the major respects in which the tests differ, are given in Table III.

It is readily apparent from the data in Table III that the low velocity torch test provides discrimination among gum vulcanizates based on different polymers whereas the high velocity test provides no discrimination. All specimens tested in the low velocity flame charred to varying degrees. It is believed that the amount, type and strength of the char determined the length of time required for heat to penetrate the specimens. In the higher velocity test, however, no visible char was formed on any of the specimens.

TABLE II

COMPOUND FORMULATIONS

Compounding Ingredients	Parts By Weight — Formula Numbers for Basic Series: M10E	N139	N141	N141C	N141C3	N141C3D3	N141C3D4	N141C3D5	Z40	Z56C5	Z101
Polychloroprene	100										
55/45 Butadiene/acrylonitrile		100	100	100	100						
65/35 " "						100					
80/20 " "							100				
Butadiene/acrylonitrile-polyvinyl chloride blend								100			
Methyl vinyl silicone									100		
Methyl phenyl vinyl silicone										100	
Vinylidene fluoride/hexafluoropropylene											100
Stearic acid	.5	1.5	2		2	2	2	2			
Zinc oxide	5	5	5		3	3	3	3			
Magnesium oxide	4										15
Phenyl-beta-naphthylamine	2										
Sulfur		2			3	3	3	3			
Benzothiazyl disulfide		1			1.2	1.2	1.2	1.2			
Tetramethyl thiuram disulfide		.5	3		.12	.12	.12	.12			
Symmetrical Di-beta-naphthyl-p-phenylenediamine		3									
Di-tert-butyl peroxide									1		
Dicumyl peroxide (40% active)										1.5	
Hexamethyleneimine											5

Fillers as indicated in applicable tables.

Compound Z40 press cured 30 minutes @153°C, post cured in an air oven 6 hours @232°C.
Compound Z56C5 press cured 10 minutes @135°C, post cured in an air oven 8 hours @190°C.
Compound Z101 press cured 35 minutes @138°C, step cured in an air oven 1 hour @100, 121, 149, 177°C, post cured 24 hours @204°C.
All other compounds press cured 35 minutes @153°C.

TABLE II (Cont.)

Compounding Ingredients	Parts By Weight — Formula Numbers for Basic Series: S77	S77C1	S77C1D and S77C1D4	S77C1D1	S77C1D5	S77C3	S77C4D2	S77C4D3
76.5/23.5 Butadiene/styrene	100	100				100		
60/40 Butadiene/styrene			100					
Cis 1,4 Polybutadiene				100	100			
High Viscosity Liquid Butadiene/styrene							100	
Low Viscosity Liquid Butadiene/styrene								100
Stearic acid	2	2	2	2	2	2		
Zinc oxide	3	3	3	3	3	3		
Sulfur	1.75	3	3	3	3	1.5	12	12
Symmetrical Di-beta-naphthyl-p-phenylenediamine	1	1	1	1	1	1		
Benzothiazyl disulfide		1.2	1.2	1.2	1.2	.5	4	4
Tetramethyl thiuram disulfide		.12	.12	.12	.12			
Zinc diethyldithiocarbamate							1.1	1.1

Fillers as indicated in applicable tables.

TABLE III

THE EFFECT OF FLAME TEMPERATURE AND GAS VELOCITY ON THE INSULATING ABILITY OF GUM VULCANIZATES

RIA Formula No.	Polymer Type	Low Velocity Test	ASTM Proposed High Velocity Test
	Approximate flame temp., °C.	2900	3300
	Total gas flow rate, SCFH	34	224
		Time to Reach Backside* Temperature of 200°C, Sec.	
Z101	Vinylidene fluoride/ hexafluoropropylene	120	7
M10EF1	Polychloroprene	48	7
N139	55/45 Butadiene/acrylo- nitrile	17	8
S77F	76.5/23.5 Butadiene/ styrene	14	7

*All specimens were 0.250 ± 0.005" thick. All results are the average of two tests. Tests were reproducible to within ±5 percent.

It is assumed that if char was formed, it was immediately blown away by the high velocity flame. Thus, in the newer test, all specimens were penetrated by the heat of the flame very rapidly and at equal rates.

Many investigators have reported that the efficacy of case insulation materials depends to a large degree upon the ability of the predominant polymeric ingredient to form low molecular weight gases. The gases add to the insulation efficiency by absorbing heat while flowing through the charred layer, through the process termed "transpirational cooling". No investigator, however, has formed definite conclusions as to which polymers provide optimum transpirational cooling when insulation is burned under the conditions of the torch test or those of actual use. Lacking this information, and realizing that the torch test was of no value in discriminating among polymers on the basis of tests on gum vulcanizates, the selection of the polymers for use in a study of filled vulcanizates became somewhat arbitrary. The two polymer types chosen for the major portion of this study, butadiene/styrene (SBR) and butadiene/acrylonitrile (NBR), were selected because of their current use in commercial insulations, their compatibility with a wide variety of fillers, low densities and low cost.

The torch evaluation results for vulcanizates based on SBR and containing fillers are given in Table IV. The data are arranged into groups, according to the types of fillers used. Choice of fillers was made on the basis of inherent heat resistance, ability to reinforce rubber, capacity to absorb heat during change in state or ability to form highly crosslinked systems.

Before analyzing the data of this report, it is important that the reader understand the significance of the performance index and the erosion rate and to be aware of the relationship between these test criteria. It should be apparent that a material which is a good thermal insulator will require a long period of time to attain a backside temperature of 200°C. and it will, therefore, show a high index. Its erosion rate will usually be low but the relationship between P_{200} and E will not necessarily be proportional, because the two values are determined at different points in time. Two materials having equal P_{200} values may exhibit grossly different E rates, depending upon their performance after the 200°C. temperature is reached. For example, one material may have a high coefficient of thermal conductivity but may be very resistant to flame penetration and erosion, in which case it will exhibit a poor (low) P_{200} but a good (low) E rate. This situation is best exemplified

TABLE IV

TORCH TEST DATA FOR FILLED SBR VULCANIZATES

FIBROUS FILLERS**

RIA Formula No.	Type of Filler	Amount, PHR*	P200	E.	Elong. %	Tensile Strength, psi
S77C1F22	Chrysotile long fiber asbestos	100	51***	5***	55	1050
S77C1F52	Chrysotile long fiber asbestos	50	38	7	95	425
S77C1F56	Acrylic fiber	100	28	13	-	-
S77C1F37	Chopped glass	100	26	10	140	190
S77C1F58	Chrysotile med. fiber asbestos	50	21	15	135	460
S77C1F104	Ceramic fiber	100	19	15	325	220
S77C1F57	Chrysotile med. fiber asbestos	100	18	14	80	800
S77C1F30	Potassium titanate	100	18	15	200	920
S77C1F21	Chrysotile asbestos floats	100	14	18	425	560
S77C1F76	Long staple aluminum silicate	100	12	22	235	170
S77C1F62	Chrysotile asbestos floats	50	12	28	375	360
S77C1F28	Chopped aluminum silicate	100	11	25	285	325
S77C1F2	Chopped aluminum silicate	50	8	41	470	160

*PHR represents parts by weight per 100 parts of rubber.

**All compounds except those containing acrylic fiber and asbestos floats were mixed with mill roll gear ratio 1:1 rather than the standard (ASTM-D-15) 1.4:1 ratio, in an attempt to preserve fiber length.

***Average of 15 tests.

TABLE IV (Cont.)

RESINOUS FILLERS

RIA Formula No.	Type of Filler	Amount, PHR*	P_{200}	E.	Elong. %	Tensile Strength, psi
S77C1F34	Phenol formaldehyde #1	100	52	6	too brittle to test	-
S77C1F49	Phenol formaldehyde #2	100	44	6	100-500	240
S77C1F43	Phenol furfural	100	40	4	65	260
S77C1F75	Phenol furfural	125	37	3	-	-
S77C1F50	Phenol formaldehyde #2	50	32	11	120	180
S77C1F51	Phenol formaldehyde #1	50	28	14	135	300
S77C1F74	Phenol furfural	75	26	9	130	150
S77C1F31	Phenol formaldehyde (hollow sphere)	100	14	24	65	240
S77C1F45	Phenol formaldehyde (oil modified)	100	14	25	380	230
S77C1F73	Phenol furfural	50	14	26	265	180
S77C1F112	Phenol furfural	25	12	28	305	280
S77C1F46	Phenol formaldehyde #3	100	8	41	1270	90

*PHR represents parts by weight per 100 parts of rubber.

THIS

PAGE

IS

MISSING

IN

ORIGINAL

DOCUMENT

TABLE IV (Cont.)

MISCELLANEOUS FILLERS

RIA Formula No.	Type of Filler	Amount, PHR	P_{200}	E.	Elong. %	Tensile Strength, psi
S77C1F44	Pentaerythritol	100	36	7	5	100
S77C1F6	Med. thermal carbon black	50	27	12	370	890
S77C1F39	Powdered polyamide plastic	100	18	20	70	110
S77C1F24	Magnesium fluoride	100	15	18	480	660
S77C1F42	Powdered sugar	100	13	24	470	160
S77C1F29	Potassium silicate	100	11	24	470	740
S77C1F40	Sodium silicofluoride	100	11	24	290	140
S77C1F35	Med. thermal carbon black	100	11	26	275	1700
S77C1F25	Potassium oxalate	100	11	27	130	80
S77C1F33	Powdered copper	100	10	17	525	700
S77C1F72	Magnesium silicate	200	10	24	775	610
S77C1F71	Magnesium silicate	100	10	26	645	540
S77C1F32	Boron carbide	100	9	28	340	340
S77C1F23	Lithium fluoride	100	9	30	420	440
S77C1F41	Powdered molybdenum	100	6	38	270	170

by the very hard, rigid materials known as carbon-graphites. Typical rubber based insulation containing less than 50 PHR of carbon black or silica fillers will exhibit a poor P_{200} as well as a poor erosion rate. For the purposes of this study, it was decided that only those insulation materials having indices over forty and erosion rates lower than five were worthy of further evaluation.

Examination of Table IV indicates that of all the vulcanizates in the first group, those containing chrysotile long fiber asbestos showed the best insulation properties. The good flame resistance of these vulcanizates is attributed to the fact that the asbestos filled vulcanizates formed profuse, strong chars which remained attached to the test specimens during the entire test, thereby insulating the substrate material against the heat of the torch. Vulcanizates containing shorter fiber length asbestos also formed large amounts of char but these chars were weak and spalled off under the impact of the high velocity gases. It is interesting to note the tensile strength values of the fiber-containing vulcanizates. The tensile value of the compound containing 100 PHR long fiber asbestos is the highest of the group, indicating that perhaps there is some correlation between tensile strength and ability to form strong char. The correlation is far from absolute, as evidenced by the fairly high tensile strength but poor performance imparted by potassium titanate. It is important at this point to note the useful temperature limits for chrysotile asbestos, ceramic and aluminum silicate fibers. The values are 815, 1140 and 1250°C., respectively. Thus, the least heat resistant fiber produces the best insulation, when all three are compared in SBR vulcanizates at equal weights. This information lends some credence to the belief that the superiority of asbestos as a filler in rubber-based insulation is due in part to its inherent strength. Those vulcanizates which contain brittle fibers such as chopped glass, ceramic or aluminum silicate, all had low tensile strengths, probably because of the cutting action of the fillers when under tension.

In the second group of fillers in Table IV, it is noted that only three of the six phenolic resins which were evaluated showed any promise as fillers for SBR based insulation. The vulcanizates containing 100 PHR of the phenol formaldehyde resins 1 and 2* and the phenol furfural resin were the only ones to exhibit good torch performance. However, the vulcanizate containing 100 PHR resin #1 was very brittle and this resin is, therefore, considered unsatisfactory for use with SBR. Poor dispersion of resin is indicated by the large

*For trade names see Code Sheet at end of report.

variation in ultimate elongation in the case of the phenol formaldehyde resin #2. The phenol furfural resin appears to be the most suitable of this group of fillers for use with SBR.

None of the oxides showed promise as fillers for SBR. Most of the vulcanizates of this group burned with a "popping out" of the filler. The compound containing hydrated silica was the only one to form a char but the char spalled rapidly. Again, as in the case of the fibrous fillers, there appears to be correlation between the ability of a filler to reinforce the rubber and the ability of the rubber to form a char.

Although none of the group of miscellaneous fillers imparted good torch resistance, two are of interest. The low but nonetheless significant effectiveness of pentaerythritol may be caused by its interaction with the rubber. The very low elongation of this vulcanizate indicates a high degree of crosslinking, perhaps caused by the large number of reactive sites and the molecular symmetry of pentaerythritol. The vulcanizate containing 100 PHR of carbon black showed surprising data; high tensile strength but poor torch performance. The explanation to this somewhat anomalous behavior is not known, but may be due to the fact that carbon black burns.

The study of single fillers used in SBR vulcanizates was followed by work on combinations of fillers in this polymer, as reported in Tables V through VII, inclusive.

Table V provides torch data for SBR-based compounds containing various combinations of long fiber chrysotile asbestos* and a phenol furfural resin. These fillers had provided good insulation to SBR vulcanizates when used separately, as shown by the data for the two control compounds. The use of these fillers in combination provided only marginal improvement in torch performance. The best compound, containing 75 PHR of asbestos and 50 PHR of resin, had a higher P_{200} value then that of the controls but it showed only little improvement in erosion rate.

The last three entries of Table V are performance data for compounds each containing 100 PHR of asbestos and of phenolic resin, but each based upon a different polymer. There is essentially no difference in P_{200} for these compounds but the erosion rates differ significantly, the compound containing the 60/40 butadiene/styrene polymer having the lowest E rate and the one containing the 76.5/23.5 ratio polymer having the highest rate. These differences may be

*In the remaining portions of this report the word "chrysotile" will be omitted from "long fiber chrysotile asbestos".

TABLE V

TORCH TEST DATA FOR SBR VULCANIZATES CONTAINING ASBESTOS AND PHENOLIC RESIN

RIA Formula No.	Long Fiber Asbestos	Phenol Furfural	P_{200}	E.	Elong. %	Remarks
S77C1F22	100	-	51	5	55	Control
S77C1F43	-	100	40*	4*	65	Control
S77C1F110	25	50	42	6	130	
S77C1F107	25	75	43	7	30	
S77C1F108	25	100	48	6	5	Elong. measured at 1"/min.
S77C1F105	50	50	52	6	60	
S77C1F113	50	75	48	5	80	
S77C1F84	50	100	47	6	35	Elong. measured at 1"/min.
S77C1F106	75	25	53	4	100	
S77C1F114	75	50	59	4	55	
S77C1F77	100	75	46	5	30	
S77C1F88	100	100	52**	5**	45	Polymer was Bd/St, 76.5/23.5
S77C1D1F88	100	100	56	4	20	Polymer was Cis 1,4 poly-butadiene #1
S77C1DF88	100	100	51	3	35	Polymer was Bd/St, 60/40

*Average of four tests.

**Average of sixteen tests.

TABLE VI

TORCH TEST DATA FOR SBR VULCANIZATES CONTAINING CERAMIC FILLERS

	Types and Amounts (PHR) of Fillers										
RIA Formula No.	Long Fiber Asbestos	Al_2O_3	Hydrated SiO_2	TiO_2	MgO	Fe_2O_3	CaO	P_{200}	E.	Elong. %	Remarks
S77C1F78	50	70	26	2.5	0.5	0.5	0.5	40*	6*	190	Sl. spalling.
S77C3F78	50	70	26	2.5	0.5	0.5	0.5	25	8	575	Reduced quantities of rubber curatives.
S77C1F16			100					25	12	325	
S77C1F86		70	26	2.5	0.5	0.5	0.5	17	16	795	Ceramic-type char which spalled quite readily.
S77C1F13		100						12	21	315	

*Average of six tests.

TABLE VII

THE EFFECT OF POTASSIUM OXALATE ON THE TORCH PERFORMANCE OF SBR VULCANIZATES

RIA Formula No.	Types and Amounts (PHR) of Fillers: Phenol Furfural Resin	Long Fiber Asbestos	Oxide Mixture*	Potassium Oxalate	P_{200}	E.	Elong. %
S77C1F80	100	50	100		52	4	7
S77C1F81	100	50	100	60	46	5	1
S77C1F84	100	50			47	6	35
S77C1F83	100	50		60	54	5	**
S77C1F43	100				40	4	65
S77C1F95	100			60	18	19	250
S77C1F78		50	100		40	6	190
S77C1F82		50	100	60	43	5	75

*The composition of this oxide mixture is given in Table VI, Formula No. S77C1F86.

**Gas bubbles formed in the vulcanized test pads; stress-strain properties could not be measured.

attributable to differences in rates of gas evolution, types of gases generated from each polymer, the fiber length of the asbestos, or the viscosity of the rubber on the mill affecting fiber length.

Table VI presents torch data for compounds containing ceramic-type fillers. Among these is a compound (S77C1F86) which contains six different metallic oxides in the proportions in which they are commonly used[8] in manufacturing high-alumina fire clay. This compound represented an attempt to produce in situ a high temperature resistant refractory material. The char which resulted from the burning of this compound was, indeed, glassy but it spalled readily and performance of this compound in the flame was poor, being intermediate between a compound containing 100 PHR alumina and one with 100 PHR silica. The high elongation of the compound containing the oxide mixture was encouraging, therefore, asbestos was included with the oxide mixture in an attempt to keep the oxide char from spalling. The resulting material (S77C1F78) did indeed exhibit reduced spalling and improved torch performance. As expected, the addition of asbestos reduced the ultimate elongation. An attempt was made to increase the elongation by reducing the quantity of rubber curatives (S77C3F78), thus producing an undercure and greater elongation. The expected effect took place but unfortunately torch performance suffered.

The results in Table VII show the effect on torch performance of the addition of potassium oxalate to SBR vulcanizates. The results show that the addition of the oxalate produced rather marginal improvement in the case of the compounds containing phenolic resin and asbestos or the oxide mixture and asbestos. In the case of the compounds containing resin, asbestos and oxides or resin alone, the addition of potassium oxalate impaired torch performance. Salts such as potassium oxalate should be desirable for use in case insulation because of their potential as transpirational cooling agents and because, in general, they have relatively low densities. They have the shortcoming, however, of being hygroscopic. Their affinity for water might adversely affect the processing of compounds containing them and might also adversely affect the storage stability of the fabricated insulation.

Only a limited amount of development work was performed with butadiene/acrylonitrile (NBR) copolymers. The most noteworthy results were obtained with a 55/45 butadiene/acrylonitrile, which was selected because the higher nitrile-containing members of the NBR class are more compatible with phenolic resins. The results of work with this NBR polymer

are given in Table VIII. The first two compounds listed have higher performance values and lower erosion rates than those of any of the other compounds described in this report and are the best insulation materials, on the basis of the torch screening test, developed by the Rock Island Arsenal Laboratory to date. In comparing the data for these two compounds to the data for similar compounds based on SBR (see Table V, F77 and F78), it appears that within the particular polymer-resin-asbestos combination in question, the use of NBR provides insulation materials superior to those in which SBR is the rubber polymer. This apparent superiority of NBR over SBR may be due to the better resin compatibility of the former. Apparent differences between the thermal insulation properties of the SBR and NBR will be discussed at greater length later in this report.

Formula N141CF of Table VIII differs from N141F in that the rubber curatives were omitted, in an attempt to provide an undercure for the rubber portion of the compound, thereby increasing the ultimate elongation of the vulcanizate. The elongation did not increase but the torch performance became poorer. This is an important point. From the low elongation of compound N141F, it may be assumed that the matrix is predominantly plastic, rather than rubber, in nature. This is probably the reason why the presence or absence of rubber curatives had little effect upon the stress-strain properties of the compound. Nevertheless, for some reason as yet not completely understood, the rubber curatives had an influence upon the performance of the compound in the torch test. Apparently the degree of crosslinking of the rubber, even though rubber is not the predominant ingredient, is important.

The last compound of Table VIII is the same as the first with the exception that it contains potassium oxalate. This salt again proved to be detrimental, as shown by the lower index and higher erosion rate of the vulcanizate containing it.

In an attempt to utilize better the strength of fibrous materials, insulation specimens were prepared by forming laminates of asbestos cloth and rubber and of an organic heat resistant cloth (see code sheet) and rubber. In some cases, compounded rubber was sheeted out and placed between layers of the cloth. In other cases the compounded rubber was applied onto one side of the cloth by means of a two-roll calendar. In one instance, the rubber was dissolved in acetone, the cloth was soaked in the rubber solution and the coated cloth was air and vacuum dried. In all cases the plied-up layers were placed in a mold and cured under the same conditions as

TABLE VIII

TORCH TEST DATA FOR FILLED VULCANIZATES BASED ON NBR

RIA Formula No.	Types and Amounts (PHR) of Fillers: Phenol Furfural Resin	Long Fiber Asbestos	Potassium Oxalate	P_{200}	E.	Elong. %	Tensile Strength, psi
N141F	100	100	-	77*	2.5*	10	2400
N141F1	100	75	-	73	2.8	10	3410
N141F2	100	50	-	60	3.0	30	1880
N141CF	100	100	-	55	2.8	10	2880
N141F4	100	100	60	48	4.5	**	**

*Average of six tests.

**This vulcanizate did not cure properly because of the presence of gas. Stress-strain properties were not determined.

were used for nonlaminated specimens. Table IX lists the major constituents, methods of fabrication and torch test data for the laminates.

None of the laminates of Table IX performed well in the screening test. Although P_{200} values are not available, it is estimated from the approximated specimen densities that the indices would range from 60 to 20. Sixty is a reasonably good index, however, all of the laminates delaminated during the torch test. The specimen in which the fabric was coated by being dipped in a solution of the rubber represented an attempt to provide good rubber to fabric adhesion. This specimen, however, delaminated as readily as did the others. A comparison of the effectiveness of laminated and nonlaminated specimens can be made in only one instance. The laminate containing nine layers of asbestos cloth is comparable in composition to the compound (S77C1F84, Table VII) containing 50 PHR long fiber asbestos. The time to 200°C for the nonlaminar compound was 43 and the erosion rate was 6, therefore, it is obvious that the laminated compound showed poorer torch performance.

Experiments were conducted in an attempt to verify the postulate that the effectiveness of insulation which contains asbestos is related to the size of the asbestos particles or fibers. Table X summarizes data presented earlier in this report for SBR compounds each containing 100 PHR of a different particle or fiber size of asbestos, ranging from fine powder to long fibers. It is apparent from the data that the longest fiber asbestos provides the best insulation. The data of Table XI further proves the superiority of long fiber over short fiber asbestos. All four entries in this table are for the same compound (S77C1F88, Table V) containing 100 PHR each of long fiber asbestos and phenol furfural resin. The compounds differ in the extent to which they were mill mixed. The first compound was mixed with the mill rolls as far apart as possible without losing continuity of the banded rubber. In this manner maximum asbestos dispersion with minimum fiber breakdown was achieved. After mixing, a portion of the rubber was cured into torch specimens. The remainder of the rubber was then further milled by end over ending 10 times. A portion of this mix was removed and cured. The third and fourth compounds received an additional 10 and 20 end over ends, respectively. The rubber which received the least mixing had long asbestos fibers clearly visible on the surface of the cured specimens whereas the rubber which had received the most mill mixing had no visible fibers on the surface. The data of Table XI clearly show the superiority of the compound which had received the least mixing and thus containing the longest fibers. Both Tables X and XI show

TABLE IX

TORCH TEST DATA FOR RUBBER CLOTH LAMINATES

RIA Formula No.	Polymer Type	Major Constituents, PHR	Type of Cloth and No. of Layers	Fabrication Method	Time To Reach 200°C, seconds*	Erosion Rate, E
N139F2	65/35 butadiene/ acrylonitrile	Hydrated silica, 60	Organic heat resistant - 5	Cloth not calendared	49	5
N139F3	"	Hydrated silica, 60 - Phenol formaldehyde resin #1, 120	Organic heat resistant - 5	"	34	7
S77C1F43	76.5/23.5 butadiene/ styrene	Phenol furfural resin, 100	Open weave asbestos - 9	Cloth soaked in rubber solution	33	7
S77C1F43	"	"	Open weave asbestos - 9	Cloth calendared	33	7
S77C1F43	"	"	Organic heat resistant - 13	"	26	8
S77C1F	"	None (gum)	Organic heat resistant - 17	"	14	17

*The performance indices could not be calculated because the densities of the laminates were not measured. Times to 200°C are corrected for specimen thickness.

TABLE X

THE EFFECT OF ASBESTOS PARTICLE SIZE ON TORCH PERFORMANCE

RIA Formula No.	Approximate Particle or Fiber Size	P_{200}	E.	Tensile Strength, psi
S77C1F22	0.18 - >0.5"	51	5	1050
S77C1F57	0.08 - 0.18"	18	14	800
S77C1F21	<0.08"	14	18	560
S77CF71	8 microns	10	26	540

TABLE XI

THE EFFECT OF DEGREE OF MILLING ON THE TORCH PERFORMANCE OF VULCANIZATES CONTAINING ASBESTOS

Extent of Milling*	P_{200}	E.	Tensile Strength, psi
Minimum	59	3	2250
10 additional end over end	48	5	2280
20 additional end over end	44	5	1090
Maximum 30 additional end over end	34	7	Not measured

*Compound used in this study was S77C1F88. See Table V for composition. All milling was performed with the ASTM standard roll gear ratio of 1.4:1. All results are the average of four tests.

good correlation among the variables of tensile strength, particle size (or extent of milling) and torch performance.

Although long fiber asbestos imparts good oxyacetylene torch resistance to rubber based vulcanizates, its rather high density (2.4 - 2.6) is a distinct disadvantage. In an effort to reduce the weight of asbestos-containing compounds, a study was made to determine the minimum amount of asbestos which would provide optimum torch resistance. The study was made with three polymers of the SBR and NBR types. A similar study was conducted with a hydrated silica filler (density 1.95). All compounds were mill mixed under the previously described conditions which optimize the retention of filler structure. Test data, shown in Table XII, clearly indicate that for each of the polymers investigated, there is a level of asbestos concentration which imparts optimum resistance to the screening test. Surprisingly, this level is approximately the same, 60 PHR, in each polymer. Asbestos loadings greater than 60 PHR do not provide better insulation. It is believed that the ratio of the concentrations of rubber and asbestos is very important to the quality of the insulation. A certain proportion of asbestos is required to provide a thermally resistant char but a certain proportion of rubber is necessary to serve as a source of cooling gases.

The data of Table XII also show that 40 PHR of hydrated silica appears to be an optimum loading for the polymers investigated. The data further reveal a most interesting point, namely, that for the compounds which contain the optimum levels of asbestos or silica (60 and 40 PHR, respectively), those based on SBR are superior to those based on NBR. As noted previously, this difference could be due to the varying degrees of efficiency in which the polymers act as transpirational cooling agents. On the other hand, the difference could be due to the physical nature of the polymers. For example, the 55/45 butadiene/acrylonitrile polymer is much tougher, harder and more difficult to process than is the 76.5/23.5 butadiene/styrene polymer. It is quite possible that during the addition of asbestos to these two polymers on the mill, greater shearing forces are exerted on the asbestos in the case of the former polymer, resulting in an NBR-asbestos compound containing shorter fibers than are present in the SBR-asbestos compound. It has already been shown that the shorter asbestos fibers lead to inferior insulation.

To study further the possible effect of polymer processability on the insulation effectiveness of vulcanizates containing asbestos, vulcanizates of nine different polymers, each compounded with 60 parts of long fiber asbestos, were prepared and tested in the torch. The solid polymers were

TABLE XII

THE EFFECT OF FILLER LEVEL ON TORCH PERFORMANCE

Polymer Type	Long Fiber Asbestos, PHR 20 P_{200}	20 E	40 P_{200}	40 E	60 P_{200}	60 E	80 P_{200}	80 E	100 P_{200}	100 E
76.5/23.5 butadiene/ styrene*	45	7	46	6	47	5	45	5	51	5
65/35 butadiene/ acrylonitrile**	28	11	39	8	38	8	37	7	35	7
55/45 butadiene/ acrylonitrile***	32	10	38	8	38	7	35	7	36	7

Polymer Type	Hydrated Silica, PHR 20 P_{200}	20 E	40 P_{200}	40 E	60 P_{200}	60 E
76.5/23.5 Bd/St*	14	22	37	8	23	13
65/35 Bd/Ac**	22	15	33	10	25	11
55/45 Bd/Ac***	20	16	25	10	25	11

*Basic formulation - S77C1
**Basic formulation - N141C3D3
***Basic formulation - N141C3
All results are the average of 4 tests.

mixed in the usual manner. The liquid polymers, their curatives and all but about two thirds of the asbestos, were mixed by hand stirring. The mix was too viscous at this point to permit the addition of the remainder of the asbestos by hand mixing; therefore, it was added by mill mixing. Even though the standard roll gear ratio of 1.4:1 was used, very little shearing action took place during the final mill mixing because the mill rolls were set about 1/2 inch apart and the compound was very soft. Table XIII gives the results of this work and also includes a qualitative evaluation of the processing characteristics of the polymers investigated. The data show excellent agreement between ease of processability and P_{200} and E values, thereby indicating that the soft, smooth, easily milled polymers, such as the liquid polymers and the first few solid polymers listed in Table XIII, probably do not cause asbestos fiber breakdown to the extent that the rougher, harder polymers do. Polybutadiene probably furnished poor insulation because it is a difficult polymer to process, not by virtue of its toughness but because of its weakness and tendency to crumble. Polymers which do not band well, but crumble on the rolls, usually must be milled with a tight nip, thereby increasing shearing forces which lead to ultimate fiber breakdown.

Table XIII also lists the behavior of each vulcanizate during burning in the screening test. Those compounds which had high performance indices and low erosion rates showed little or no evidence of loss of char or "spalling" during the torch test. Conversely, the poorer performing compounds spalled readily. Throughout this entire study, spalling has been noted to occur in those compounds in which the asbestos fibers are of short length. Here again is evidence that the integrity of the fiber must be retained in order to achieve optimum insulation. For example, those compounds based on the liquid SBR polymers and containing asbestos loadings as low as 40 PHR provide more efficient insulation materials than result from the use of 60 PHR asbestos with conventional solid SBR polymers. Undoubtedly the long fibers of asbestos suffer less breakage when mixed with liquid polymers than when milled with solid polymers.

In view of the good insulation materials developed from the liquid and the easy processing solid polymers in combination with 60 parts of long fiber asbestos, these polymers were further exploited by combining them with other types of fillers or lesser amounts of asbestos as noted in Table XIV. Some excellent materials resulted.

The second entry of Table XIV is one of special interest. The polymer in this case is a blend of a butadiene/acrylonitrile (NBR) and polyvinyl chloride (PVC). The excellent

TABLE XIII

THE EFFECT OF POLYMER PROCESSABILITY ON THE TORCH PERFORMANCE OF VULCANIZATES CONTAINING 60 PARTS OF LONG FIBER ASBESTOS

RIA FORMULA NO.	POLYMER TYPE	P_{200}	E.	ELONG., %	TENSILE STRENGTH, psi	POLYMER PROCESSING CHARACTER-ISTICS	BEHAVIOR OF SPECIMEN ON BURNING
N141C3D5F5	Blend of poly-vinyl chloride & butadiene/acrylo-nitrile	59	4	45	2450	Excellent - smooth, soft bands well	No spalling slight blowing
N141C3D4F5	80/20 butadiene/ acrylonitrile	57	5	90	1020	Excellent - Fairly smooth & soft band	No spalling
S77C4D3F119	Liquid SBR Viscosity: 500-2500 poises	56	4	20	1800	Excellent - Very soft, sticky band	No spalling
S77C4D2F119	Liquid SBR Viscosity: 7500-12500 poises	53	3	30	2200	Excellent - Very soft, sticky band	No spalling
S77C1D4F119	60/40 butadiene/ styrene	50	5	80	830	Good	Slight spalling at beginning
S77C1F119	76.5/23.5 butadiene/ styrene	47	5	85	1190	Good	Slight spalling at beginning
S77C1D5F119	Cis 1,4 poly-butadiene #2	42	7	75	250	Very poor - low strength, crumbles	Hvy. spalling at beginning
N141C3F5	55/45 buta-diene/acrylo-nitrile	38	7	75	3330	Poor - hard & tough, bands poorly	Hvy. spalling throughout burning
N141C3D3F13	65/35 butadiene/ acrylonitrile	38	8	195	1320	Poor - hard & tough, bands poorly	Hvy. spalling throughout burning

All results are the average of 4 tests.

TABLE XIV

INSULATION MATERIALS BASED ON EASY PROCESSING POLYMERS

RIA FORMULA NO.	POLYMER TYPE	TYPE AND AMOUNT (PHR) OF FILLER	P_{200}	E	ELONG., %	TENSILE STRENGTH, psi
S77C4D2F1	High viscosity liquid SBR	Long fiber asbestos - 50	69	3	40	2450
N141C3D5F19	NBR, PVC blend	Long fiber asbestos - 40 Hydrated silica - 20	67	3	75	2200
S77C4D3F1	Low viscosity liquid SBR	Long fiber asbestos - 50	67	3	30	2130
S77C4D2F118	High viscosity liquid SBR	Long fiber asbestos - 40	65	4	35	1660
N141C3D5F20	NBR, PVC blend	Long fiber asbestos - 60 Hydrated silica - 40	65	4	55	3930
S77C4D3F118	Low viscosity liquid SBR	Long fiber asbestos - 40	61	4	30	1170
N141C3D5F5	NBR, PVC blend	Long fiber asbestos - 60	59	4	45	2450
S77C1F128	76.5/23.5 SBR	Long fiber asbestos - 40 Ultra fine silica - 20	58	4	195	950
S77C1F127	76.5/23.5 SBR	Long fiber asbestos - 40 Hydrated silica - 20	53	5	160	910
S77C1F126	76.5/23.5 SBR	Long fiber asbestos - 40 Ultra fine carbon black - 20	52	4	220	900
S77C1F119	76.5/23.5 SBR	Long fiber asbestos - 60	47	5	85	1190

All results are the average of 4 tests.

torch performance of the vulcanizate based on this polymer may be due, in part, to the ease with which the long fiber asbestos is incorporated into the rubber, but may also be due to the presence of the PVC. It is known that polyvinyl fluoride, a polymer similar in many respects to PVC, volatilizes completely upon pyrolysis and does not form a char. Perhaps PVC acts similarly. If this is true, the blend of NBR and PVC would produce a larger volume of gases than would NBR alone, because undoubtedly NBR polymer produces some char rather than volatilizing completely. This increased amount of gas might produce a large enough cooling effect to account for the superiority of the NBR/PVC blend. It was noted after the torch burning of the NBR/PVC compound containing asbestos and silica (N141C3D5F19) that the specimen had blown and expanded. This behavior was not observed with any other similarly filled polymer compositions, thus indicating that the NBR/PVC blend did, perhaps, produce greater volumes of gas than did compounds based on other polymers.

The use of fine particle size carbon black or hydrated silica in conjunction with asbestos improved torch performance over that obtained with asbestos alone. Compounds N141C3D5F19 and N141C3D5F5 show this comparison for the compounds containing the NBR/PVC blend and the last four compounds of Table XIV show the comparison for vulcanizates based on a solid SBR. The reason for this apparent synergism is not understood.

Rubber manufacturers quite recently have been recommending the use of silicone rubber for rocket motor thermal insulation. Examination of manufacturer's reports shows that their recommendations are based on data obtained by the use of low velocity, low heat flux torch systems. A very limited study was made of insulation compounds based on methyl vinyl and methyl phenyl vinyl silicone polymers. The torch test results given in Table XV do not look promising, however, the low viscosity, almost liquid character of many of the silicone polymers, should make them very desirable as a matrix for fibrous fillers. Further evaluation of liquid silicone polymers is planned.

Several of the better insulation materials developed during the early portions of the work covered by this report were tested in static rocket motor firings. Results of the firing tests conducted by the Atlantic Research Corporation are given in Table XVI. Results for the control compound used in these tests (a commercial rubber-based material) are also included. The insulations based on liquid polymers and on the NBR/PVC blend had not been developed at the time that the motor tests were conducted, however, the torch test data

TABLE XV

TORCH PERFORMANCE DATA FOR SILICONE VULCANIZATES

RIA FORMULA NO.	POLYMER TYPE	FILLER, PHR	P_{200}	E	ELONG., %	TENSILE STRENGTH, psi
Z40F7	Methyl vinyl	Long fiber asbestos - 50	36	8	20	220
Z56C5F2	Methyl phenyl vinyl	Long fiber asbestos - 50	27	10	-	-
Z56C5F	Methyl phenyl vinyl	None	23	15	810	1670
Z56C5F4	Methyl phenyl vinyl	Hydrated silica - 20	16	27	230	840
Z56C5F3	Methyl phenyl vinyl	Hydrated silica - 40	10	29	-	-

TABLE XVI

STATIC MOTOR FIRING AND TORCH TEST DATA FOR THE BETTER INSULATION MATERIALS

RIA FORMULA NO.	POLYMER TYPE	FILLERS, PHR	P_{200}	E	ARC* MOTOR FIRING TEST DATA		ELONG., %
					CONVERGENT, mils/sec.	PERIPHERAL SLAB, mils/sec.	
N141F	55/45 butadiene/ acrylonitrile	Phenol furfural - 100 Long fiber asbestos - 100	77	3	1.6	4.8	10
Commercial Material	NBR	Phenolic resin Organic salt	77**	3**	3.1	5.0	3
S77C4D2F1	Liquid, high viscosity SBR	Long fiber asbestos - 50	69	3	-	-	40
N141C3D5F19	NBR/PVC Blend	Hydrated silica - 20 Long fiber asbestos - 40	67	3	-	-	75
S77C4D3F1	Liquid, low viscosity SBR	Long fiber asbestos - 50	67	3	-	-	30
S77C1F88	76.5/23.5 butadiene/ styrene	Phenol furfural - 100 Long fiber asbestos - 100	57	5	2.5	3.8	5
S77C1F78	76.5/23.5 butadiene styrene	Metal oxides - 100 Long fiber asbestos - 100	52	4	2.5	5.7	65

*Atlantic Research Corporation.
**Average of 17 tests.

for such insulations are also given in the table. The results of the firing tests performed by the Allegany Ballistics Laboratory were classified and are not included in this report.

It is apparent from the data of Table XVI that the motor firing test results do not correlate in all cases with the results of the torch test. The convergent motor results show all three materials which were tested to be superior to the control. However, two of these three materials had poorer torch performance than that of the control. The peripheral slab motor test results would correlate with torch test data were it not for the one value of 3.8 which is out of line. Thus the convergent test rates as best the material with the highest torch performance, but the peripheral slab test rates as best one of the poorer torch performers. Similar lack of correlation between motor and torch test results have been observed by many investigators and is not really surprising, in view of the gross differences between the conditions of the tests, namely, exposure times, temperatures, pressures and environments.

The three compounds based on liquid SBR or the blend of PVC and NBR are listed in Table XVI merely to show the relationship of their torch test values to those of the compounds which were tested in motor firings. From this relationship it would seem reasonable to expect good performance of these three materials in the motor firing tests.

DISCUSSION

It was hoped that the exploratory work covered by this report would result in definite guidelines which would establish the types of materials needed to produce superior, rubber-based case insulation. One such guideline was established, namely, that effective insulation must contain materials which will form profuse amounts of hard, tenacious, erosion resistant char. It has been shown that gum elastomers do not, by themselves, form such chars, but that these same elastomers, when combined with certain types of fillers, produce char forming vulcanizates. The most effective fillers are: (1) the fibrous materials which combine good heat resistance with inherent strength, (2) resins which form highly crosslinked networks, and (3) reinforcing materials which increase the rubber crosslinked structure. Compatibility between filler and rubber is essential in all cases.

Several important observations have resulted from this study but proof of their general applicability is lacking. These observations are as follows:

1. The degree of crosslinking of the rubber component of the insulation is important to the net efficiency of the insulation. The degree of filler reinforcement and the type and amount of rubber curatives appear to be important in this respect.

2. Certain polymers seem to produce more effective insulation than others when each is combined with equal parts of the same fibrous filler. It is not known whether this is due to the ability of certain polymers to form more char or to produce more gas than others or whether the difference is due to the ability of the polymers to mix with the fillers without breaking down the fiber structure. To answer this question it will be necessary to evaluate a large number of liquid polymers of essentially equal viscosity, in order to eliminate the variable of fiber breakdown due to shearing forces between filler and polymer.

3. There appears to be an optimum ratio between filler and polymer for optimum torch performance. It is postulated that certain proportions of a char forming ingredient (filler) as well as a gas forming ingredient (rubber) are required. Verification of this postulate should be of great value to the future development of flexible insulations.

LITERATURE REFERENCES

1. Batchelor, J.D., Vasileff, N., McCormick, S.W., and Olcott, E.L., "Development and Evaluation of Solid Propellant Rocket Motor Case Insulating Materials Systems", WADD Technical Report 60-109, Part I, June 1960.

2. Batchelor, J.D., Vasileff, N., McCormick, S.W., and Olcott, E.L., "Insulation Materials For Solid Propellant Rocket Motors", WADD Technical Report 60-109, Part II, August 1961.

3. Shapiro, L., and Hughes, C.H., "Prefabricated Flexible Internal Insulation", presented at the 2nd Symposium on Materials and Design For Rocket Insulation and Nozzles, March 1960.

4. Mihalow, F.A, Koubek, F.J., and Perry, H.A., "Ablation Test Methods For Rocket and Heat Shield Materials", NAVWEPS Report 7314, October 1960.

5. Eglin, S.B., and Jones, R.W., "Rocket Liner Program", First Quarterly Report under Contract DA-04-495-ORD-3079, 1 July to 10 October, 1960. (Confidential).

6. ASTM Standards on Rubber Products, American Society For Testing Materials, 1916 Race Street, Philadelphia, Pa. (March 1960).

7. Sale, D.H., "Evaluation of Flexible Insulation For Solid Propellant Rocket Motor Cases", RIA Technical Report No. 61-2915, 2 August 1961.

8. Kingery, W.D., "Introduction to Ceramics", John Wiley & Sons, New York, 1960.

DISTRIBUTION

	No. of Copies
A. Department of Defense	
Office of the Director of Defense Research & Engineering ATTN: Mr. J. C. Barrett Room 3D-1067, The Pentagon Washington 25, D. C.	1
Armed Services Technical Information Agency ATTN: TIPDR Arlington Hall Station Arlington 12, Virginia	10
Defense Metals Information Center Battelle Memorial Institute Columbus, Ohio	1
Solid Propellant Information Agency Applied Physics Laboratory The Johns Hopkins University Silver Spring, Maryland	3
B. Department of the Army - Technical Services	
Office Chief of Ordnance ATTN: ORDTB-Materials Department of the Army Washington 25, D. C.	1
Commanding General Aberdeen Proving Ground ATTN: Dr. C. Pickett, C&CL Aberdeen Proving Ground, Maryland	1
Commanding General Ordnance Tank-Automotive Command ATTN: Mr. S. Sobak, ORDMC-IF-2 Detroit 9, Michigan	1
Commanding General Ordnance Weapons Command ATTN: Mr. B. Gerke, ORDOW-IA Rock Island, Illinois	1

DISTRIBUTION

	No. of Copies
Commanding General U.S. Army Ordnance Missile Command ATTN Documentation & Technical Information Branch	2
Mr. R. E. Ely, ORDXM-RRS	1
Mr. R. Fink, ORDXM-RKX	1
Mr. W. K. Thomas, ORDXM	1
Mr. E. J. Wheelahan, ORDXM-RSM Redstone Arsenal, Alabama	1
Commanding General U.S. Army Ordnance Special Weapons Ammunition Command Dover, New Jersey	1
Commanding Officer Diamond Ordnance Fuze Laboratory ATTN: Technical Library Washington 25, D. C.	4
Commanding Officer Frankford Arsenal ATTN: Dr. H. Gisser, ORDBA-1330	1
Mr. H. Markus, ORDBA-1320	1
Mr. E. Roffman, ORDBA-1740 Philadelphia 37, Pa.	1
Commanding Officer Ordnance Materials Research Office Watertown Arsenal ATTN: RPD Watertown 72, Mass.	1
Commanding Officer Picatinny Arsenal ATTN: Mr. J. J. Scavuzzo, Plastics & Packaging Lab	3
Mr. D. Stein, ORDBB-DE3 Dover, New Jersey	1
Commanding Officer PLASTEC Picatinny Arsenal Dover, New Jersey	1

DISTRIBUTION

	No. of Copies
Commanding Officer Rock Island Arsenal ATTN: Materials Section, Laboratory Rock Island, Illinois	1
Commanding Officer Springfield Armory ATTN: Mr. R. Korytoski, Research Materials Lab Springfield 1, Mass.	1
Commanding Officer Watertown Arsenal ATTN: ORDBE-LX Watertown 72, Mass.	3
Commanding Officer Watervliet Arsenal ATTN: Mr. F. Dashnaw, ORDBF-R Watervliet, New York	1
Headquarters U.S. Army Signal R&D Laboratory ATTN: Mr. H. H. Kedesky, SIGRA/SL-XE Fort Monmouth, N. J.	1
Department of the Army - Other Army Agencies	
Commander Army Research Office Office Chief Research & Development ATTN: Physical Sciences Division Pentagon Washington 25, D. C.	2
C. Department of the Navy	
Chief, Bureau of Naval Weapons Department of the Navy ATTN: Mr. H. Boertzel	6
Mr. P. Goodwin Washington 25, D. C.	1

DISTRIBUTION

	No. of Copies
Department of the Navy Office of Naval Research ATTN: Code 423 Washington 25, D. C.	1
Department of the Navy Special Projects Office ATTN: SP 271 Washington 25, D. C.	1
Commander U.S. Naval Ordnance Laboratory ATTN: Code WM White Oak, Silver Spring, Maryland	1
Commander U.S. Naval Ordnance Test Station ATTN: Technical Library Branch China Lake, California	1
Commander U.S. Naval Research Laboratory ATTN: Mr. J. E. Srawley Anacostia Station Washington 25, D. C.	1

D. Department of the Air Force

U.S. Air Force Directorate of Research & Development ATTN: Lt. Col. J. B. Shipp, Jr. Room 4D-313, The Pentagon Washington 25, D. C.	1
Wright Air Development Division ATTN: H. Zoeller, ASRCEE-1-2	2
R. F. Klinger, ASRCEM-1 Wright-Patterson Air Force Base, Ohio	2
ARDC Flight Test Center ATTN: Solid Systems Division FTRSC Edwards Air Force Base, California	1

DISTRIBUTION

	No. of Copies
AMC Aeronautical Systems Center ATTN: Manufacturing & Materials Technology Division, LMBMO Wright-Patterson Air Force Base, Ohio	2
E. Other Government Agencies	
U.S. Atomic Energy Commission Office of Technical Information Extension P.O. Box 62 Oak Ridge, Tennessee	1
National Aeronautics and Space Administration ATTN: Mr. B. G. Achhammer	1
Mr. G. C. Deutsch	1
Dr. G. H. Reisig	1
Mr. R. V. Rhode Washington, D. C.	1
Dr. W. Lucas George C. Marshall Space Flight Center, M-S&M-M Huntsville, Alabama	1
Mr. William A. Wilson George C. Marshall Space Flight Center, M-ME-M Huntsville, Alabama	1
Dr. L. Jaffe Jet Propulsion Laboratory California Institute of Technology 4800 Oak Grove Drive Pasadena, California	1
F. Defense Contractors (For classified reports, the cognizant defense agency through which the report is transmitted will be included)	
Aerojet-General Corporation ATTN: Librarian P.O. Box 1168 Sacramento, California	1

DISTRIBUTION

	No. of Copies
Aerojet-General Corporation	
ATTN: Librarian	1
Mr. C. A. Fournier	1
P.O. Box 296	
Azusa, California	
Allison Division	
General Motors Corporation	
ATTN: Mr. D. K. Hanink	
Indianapolis 6, Indiana	1
ARDE-Portland, Inc.	
ATTN: Mr. R. Alper	
100 Century Road	
Paramus, N. J.	1
Atlantic Research Corporation	
ATTN: Mr. E. A. Olcott	
Shirley Highway and Edsall Road	
Alexandria, Virginia	1
Curtiss-Wright Corporation	
Wright Aeronautical Division	
ATTN: Mr. R. S. Shuris	1
Mr. A. M. Kettle, Technical Library	1
Wood-Ridge, N. J.	
Hercules Powder Company	
Allegheny Ballistics Laboratory	
ATTN: Dr. R. Steinberger	
P.O. Box 210	
Cumberland, Maryland	1
Hughes Aircraft Company	
ATTN: Librarian	
Culver City, California	1
Rohm & Haas Company	
Redstone Arsenal Division	
ATTN: Library	
Redstone Arsenal, Alabama	1

DISTRIBUTION

	No. of Copies
Tapco Group ATTN: Mr. W. J. Piper 23555 Euclid Avenue Cleveland 17, Ohio	1
Thiokol Chemical Corp. Redstone Division ATTN: Library Redstone Arsenal, Alabama	1
Republic Aviation Co. Missile Systems Division 223 Jericho Turnpike Mineola, New York	1

AD __________ Accession No. __________
Rock Island Arsenal Laboratory, Rock Island, Illinois
DAVELOPMENT OF FLEXIBLE INSULATION FOR SOLID PROPELLANT ROCKET MOTOR CASES
by R. E. Ofner and D. H. Sale

RIA Lab. Rep. 62-2366, 6 July 62, 42 p. incl. illus. tables, (DA Project No. 593-32-008, OMS Code No. 5010.11.843) Unclassified report.

The development of flexible, solid propellant rocket motor case insulation is discussed. Data are presented for insulation based primarily on butadiene/styrene and butadiene/acrylonitrile copolymers. The oxyacetylene torch test currently being standardized by the Flame Ablation Test Group of Section III-L of ASTM Committee D-20 was the principle screening tool used in the study.

Vulcanizates were compounded using a variety of fillers and filler combinations including salts, resins and fibers. The selection of
(Cont.) over

UNCLASSIFIED

1. Insulation-Materials
2. Insulating Compounds-Development
3. Rocket Motors-Materials

DISTRIBUTION: Copies obtainable from ASTIA-DSC

AD __________ Accession No. __________
Rock Island Arsenal Laboratory, Rock Island, Illinois
DAVELOPMENT OF FLEXIBLE INSULATION FOR SOLID PROPELLANT ROCKET MOTOR CASES
by R. E. Ofner and D. H. Sale

RIA Lab. Rep. 62-2366, 6 July 62, 42 p. incl. illus. tables, (DA Project No. 593-32-008, OMS Code No. 5010.11.843) Unclassified report.

The development of flexible, solid propellant rocket motor case insulation is discussed. Data are presented for insulation based primarily on butadiene/styrene and butadiene/acrylonitrile copolymers. The oxyacetylene torch test currently being standardized by the Flame Ablation Test Group of Section III-L of ASTM Committee D-20 was the principle screening tool used in the study.

Vulcanizates were compounded using a variety of fillers and filler combinations including salts, resins and fibers. The selection of
(Cont.) over

UNCLASSIFIED

1. Insulation-Materials
2. Insulating Compounds-Development
3. Rocket Motors-Materials

DISTRIBUTION: Copies obtainable from ASTIA-DSC

AD __________ Accession No. __________
Rock Island Arsenal Laboratory, Rock Island, Illinois
DAVELOPMENT OF FLEXIBLE INSULATION FOR SOLID PROPELLANT ROCKET MOTOR CASES
by R. E. Ofner and D. H. Sale

RIA Lab. Rep. 62-2366, 6 July 62, 42 p. incl. illus. tables, (DA Project No. 593-32-008, OMS Code No. 5010.11.843) Unclassified report.

The development of flexible, solid propellant rocket motor case insulation is discussed. Data are presented for insulation based primarily on butadiene/styrene and butadiene/acrylonitrile copolymers. The oxyacetylene torch test currently being standardized by the Flame Ablation Test Group of Section III-L of ASTM Committee D-20 was the principle screening tool used in the study.

Vulcanizates were compounded using a variety of fillers and filler combinations including salts, resins and fibers. The selection of
(Cont.) over

UNCLASSIFIED

1. Insulation-Materials
2. Insulating Compounds-Development
3. Rocket Motors-Materials

DISTRIBUTION: Copies obtainable from ASTIA-DSC

AD __________ Accession No. __________
Rock Island Arsenal Laboratory, Rock Island, Illinois
DAVELOPMENT OF FLEXIBLE INSULATION FOR SOLID PROPELLANT ROCKET MOTOR CASES
by R. E. Ofner and D. H. Sale

RIA Lab. Rep. 62-2366, 6 July 62, 42 p. incl. illus. tables, (DA Project No. 593-32-008, OMS Code No. 5010.11.843) Unclassified report.

The development of flexible, solid propellant rocket motor case insulation is discussed. Data are presented for insulation based primarily on butadiene/styrene and butadiene/acrylonitrile copolymers. The oxyacetylene torch test currently being standardized by the Flame Ablation Test Group of Section III-L of ASTM Committee D-20 was the principle screening tool used in the study.

Vulcanizates were compounded using a variety of fillers and filler combinations including salts, resins and fibers. The selection of
(Cont.) over

UNCLASSIFIED

1. Insulation-Materials
2. Insulating Compounds-Development
3. Rocket Motors-Materials

DISTRIBUTION: Copies obtainable from ASTIA-DSC

these fillers was based on such properties as heat stability, ability to form char, heat capacity and their known ability to reinforce rubber. As a result of these studies, a material was developed which static motor tests show to have promise as a flexible material for case insulation. This material was based on a butadiene/acrylonitrile-phenol furfural-asbestos composition.

Other promising materials which are reported are based on two types of liquid butadiene/styrene copolymers and a butadiene/acrylonitrile-polyvinyl chloride blend.

these fillers was based on such properties as heat stability, ability to form char, heat capacity and their known ability to reinforce rubber. As a result of these studies, a material was developed which static motor tests show to have promise as a flexible material for case insulation. This material was based on a butadiene/acrylonitrile-phenol furfural-asbestos composition.

Other promising materials which are reported are based on two types of liquid butadiene/styrene copolymers and a butadiene/acrylonitrile-polyvinyl chloride blend.

these fillers was based on such properties as heat stability, ability to form char, heat capacity and their known ability to reinforce rubber. As a result of these studies, a material was developed which static motor tests show to have promise as a flexible material for case insulation. This material was based on a butadiene/acrylonitrile-phenol furfural-asbestos composition.

Other promising materials which are reported are based on two types of liquid butadiene/styrene copolymers and a butadiene/acrylonitrile-polyvinyl chloride blend.

these fillers was based on such properties as heat stability, ability to form char, heat capacity and their known ability to reinforce rubber. As a result of these studies, a material was developed which static motor tests show to have promise as a flexible material for case insulation. This material was based on a butadiene/acrylonitrile-phenol furfural-asbestos composition.

Other promising materials which are reported are based on two types of liquid butadiene/styrene copolymers and a butadiene/acrylonitrile-polyvinyl chloride blend.